Electronic Supporting Information

The anionic framework Zn-MOF composed of 1D columnar SBU has high C_2H_2/CH_4 selective adsorption, dye adsorption and fluorescence sensing

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Table S1 Selected Bond Length (Å) and Angles (°).

Zn(01)-O(2A)#1	2.04(2)	Zn(01)-O(2A)#2	2.04(2)
Zn(01)-C(1A)#1	2.582(14)	Zn(01)-N21	2.182(13)
Zn(01)-C(1A)#2	2.582(14)	Zn(02)-O(1)	1.9462(11)
Zn(02)-N11	1.891(14)	Zn(02)-O22	1.942(9)
O(2A)#1-Zn(01)-O(2A)#2	141.6(15)	N21-Zn(01)-C(1A)#2	133.2(6)
N21-Zn(01)-C(1A)#1	97.8(7)	N11-Zn(02)-O22	106.9(6)
N11-Zn(02)-O(1)	107.6(5)	O22-Zn(02)-O(1)	107.5(3)
N11-Zn(02)-Zn(02)#3	84.2(5)	O22-Zn(02)-Zn(02)#3	143.9(3)
O(1)-Zn(02)-Zn(02)#3	37.45(3)	Zn(02)#5-O(1)-Zn(02)#6	105.10(7)
Zn(02)#5-O(1)-Zn(02)#3	111.70(4)	Zn(02)#6-O(1)-Zn(02)#3	111.70(4)
Zn(02)#5-O(1)-Zn(02)	111.70(4)	Zn(02)#6-O(1)-Zn(02)	111.70(4)
Zn(02)#3-O(1)-Zn(02)	105.10(7)	C21-N11-Zn(02)	128.0(10)
C11-N11-Zn(02)	128.6(12)	C11-N21-Zn(01)	119.3(10)
C31-N21-Zn(01)	134.3(10)	C12-O22-Zn(02)	111.1(8)
O(2A)-C(1A)-Zn(01)#1	50.9(13)	O(1A)-C(1A)-Zn(01)#1	73.3(8)
C(2A)-C(1A)-Zn(01)#1	66.3(14)	C(1A)-O(2A)-Zn(01)#1	101.3(16)

Symmetrical codes: #1 -x, -y+1, -z+1; #2 x+1/2, -y+1, z-1; #3 -x+1/2, -y+3/2, z; #4 -y+1/2, -x+1/2, -z+1; #5 -y+1, x+1/2, -z+1; #6 y-1/2, -x+1, -z+1.

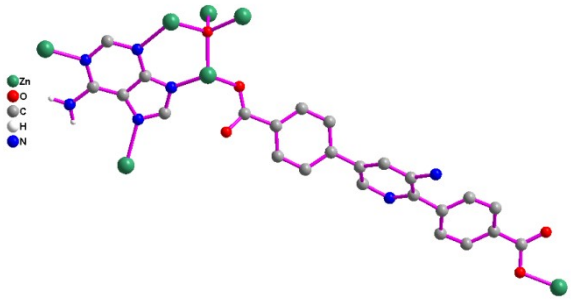


Figure S1 Coordination modes of the ligands in **Zn-MOF**.

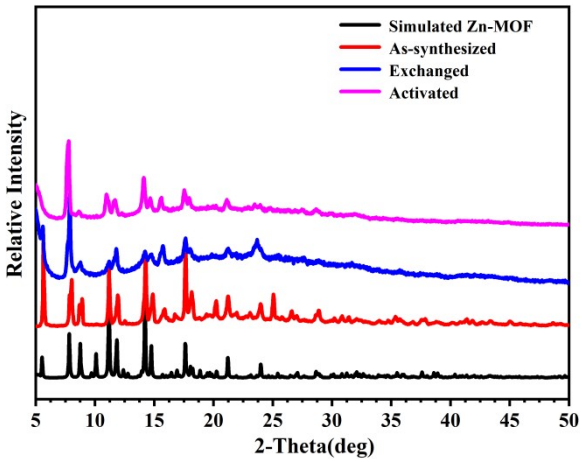


Figure S2 PXRD: Simulated, as-synthesized, exchange and activated samples.

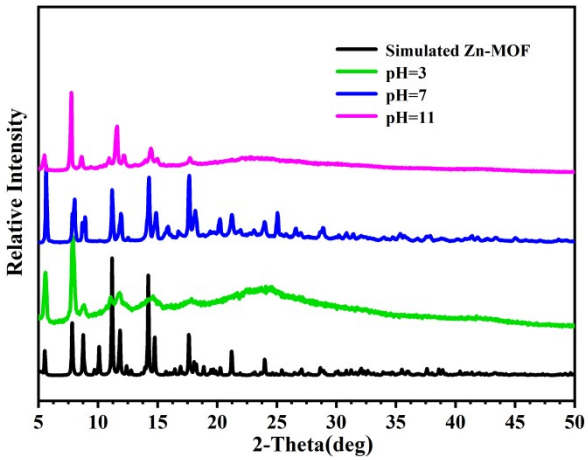


Figure S3 PXRD: Simulated, pH=3, pH=7 and pH=11 exchange activated samples.

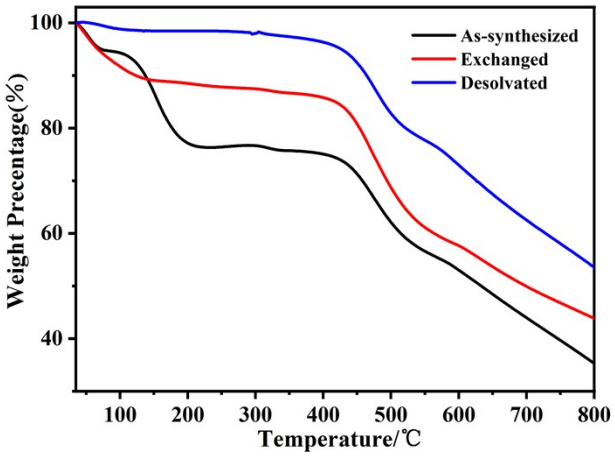


Figure S4 TGA: as-synthesized, exchanged and desolvated samples.

IAST adsorption selectivity calculation

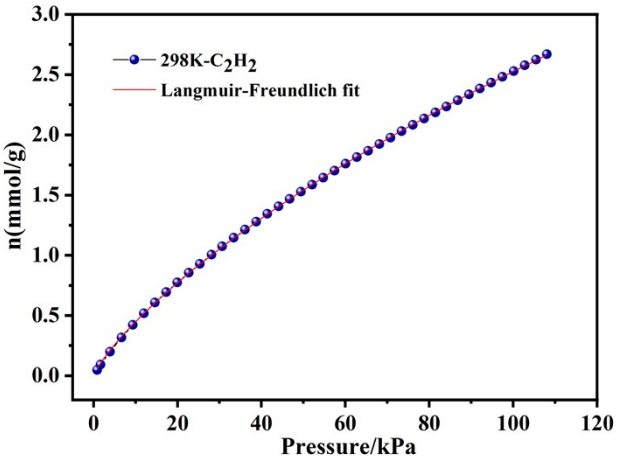
The experimental isotherm data for pure C_2H_2、C_2H_4、CO_2 and CH_4 (measured at 298 K) were fitted using a Langmuir-Freundlich (L-F) model.

$$q = \frac{a * b * p^c}{1 + b * p^c}$$

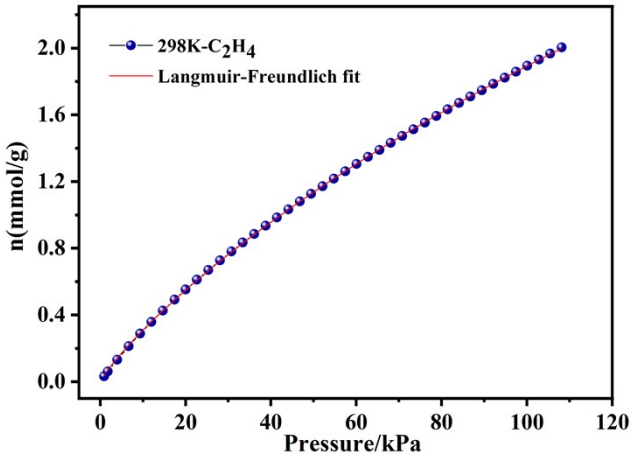
Where q and p are adsorbed amounts and pressures of component i, respectively. The adsorption selectivities for binary mixtures of C_2H_2/CH_4、C_2H_4/CH_4 and CO_2/CH_4 at 298 K, defined by

$$S_{ads} = (q_1 / q_2) / (p_1 / p_2)$$

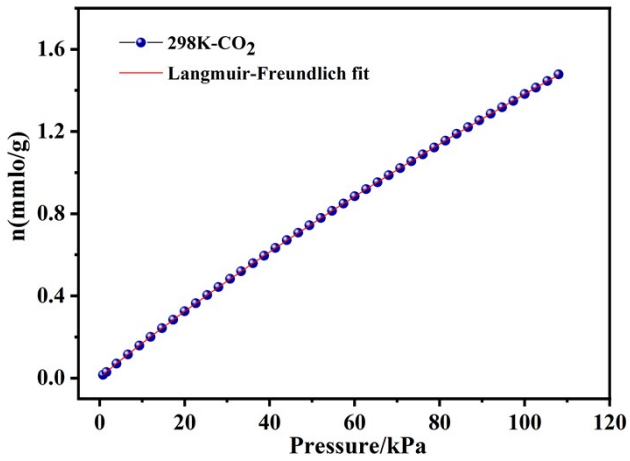
Where qi is the amount of i adsorbed and p_i is the partial pressure of i in the mixture.



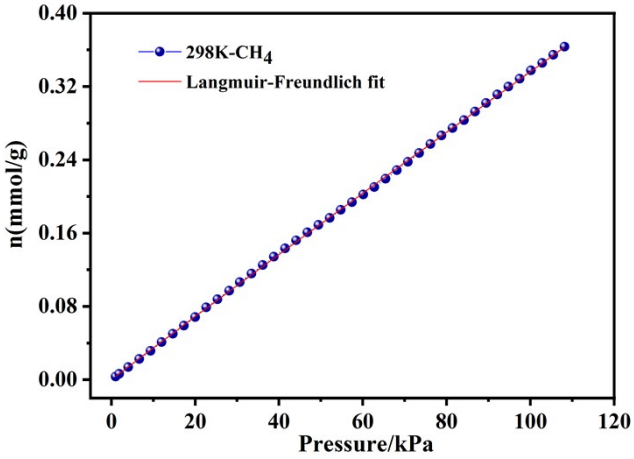
(a)



(b)



(c)



(d)

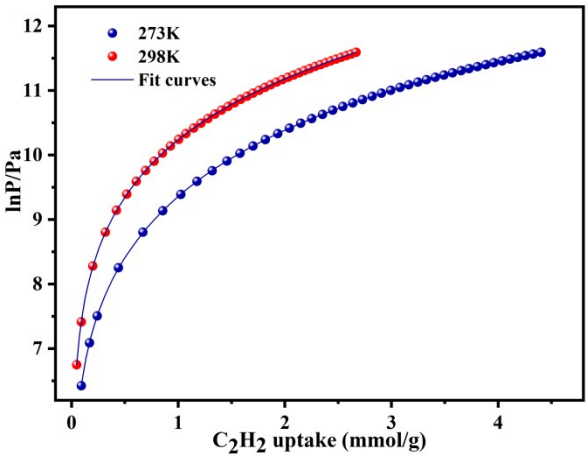
Figure S5 (a) C_2H_2 adsorption isotherms of **Zn-MOF** at 298 K with fitting by L-F model: a=16.34618, b=0.00436, c=0.18891, Chi^2=3.2826E-5, R^2=0.99994; (b) C_2H_4 adsorption isotherms of **Zn-MOF** at 298 K with fitting by L-F model: a=9.79057, b=0.00443, c=0.13344, Chi^2=1.5219E-5, R^2=0.99996; (c) CO_2 adsorption isotherms of **Zn-MOF** at 298 K with fitting

by L-F model: a=14.11683, b=0.00137, c=0.05077, Chi^2=5.64383E-7, R^2=1; (d) CH_4 adsorption isotherms of **Zn-MOF** at 298 K with fitting by L-F model: a=26.50021, b=1.33808, c=0.00879, Chi^2=1.33941E-6, R^2=0.99989.

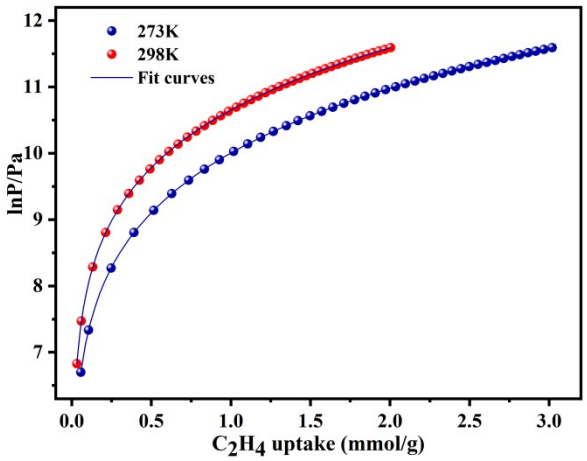
Calculation of sorption heat for C_2H_2、C_2H_4 and CO_2 uptakes using Virial 2 model

The above equation was applied to fit the combined C_2H_2、C_2H_4 and CO_2 and isotherm data for desolvated **Zn-MOF** at 273 and 298 K, where *P* is the pressure, *N* is the adsorbed amount, *T* is the temperature, *ai* and *bi* are virial coefficients, and *m* and *n* are the number of coefficients used to describe the isotherms. Q_{st} is the coverage-dependent enthalpy of adsorption and *R* is the universal gas constant.

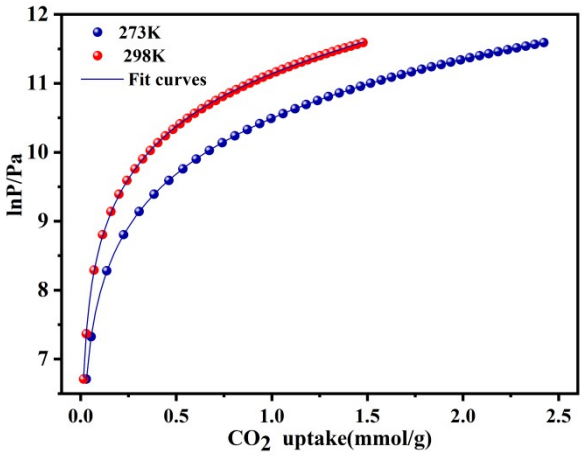
$$\ln P = \ln N + 1/T \sum_{i=0}^{m} aiN^i + \sum_{i=0}^{n} biN^i Q_{st} = -R \sum_{i=0}^{m} aiN^i$$



(a)



(b)



(c)

Figure S6 (a) Virial analysis of the C_2H_2 adsorption data at 298 K and 273 K for **Zn-MOF**. Fitting results: a0=-3286.16843, a1=512.65988, a2=-91.37345, a3=6.29229, a4=-1.14897, Chi^2=1.26889E-5, R^2=0.99999; (b) Virial analysis of the C_2H_4 adsorption data at 298 K and 273 K for **Zn-MOF**. Fitting results: a0=-2357.196, a1=324.55734, a2=-87.96432, a3=11.04662, a4=-1.21749, Chi^2=2.5328E-6, R^2=1. (c) Virial analysis of the CO_2 adsorption data at 298 K and 273 K for **Zn-MOF**. Fitting results: a0=-2254.39669, a1=-231.24997, a2=654.9978, a3=-267.66544, a4=-5.20644, Chi^2=4.83197E-5, R^2=0.99996.

Dye adsorption performance. The adsorption capacity of **Zn-MOF** for various dyes were assessed according to standard methods. The adsorption amounts (q_t (mg/g), q_e (mg/g)) and the adsorption rates (removal efficiency, R %) were calculated by E_{qs}. (1), (2) and (3), respectively:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

$$R\% = \frac{C_0 - C_t}{C_0} \times 100\% \quad (3)$$

Herein, C_0, C_t and C_e (mg L^{-1}) are the initial, any time t, and equilibrium concentrations of the organic dye in solution, respectively, V (L) represents the volume of the dye solution and adsorbent mass is m (g).

The adsorption kinetics models of pseudo-first-order and pseudo-second-order were

performed to investigate adsorption mechanism. The pseudo-first-order and pseudo-second-order models were displayed the following:

$$In(q_e - q_t) = Inq_e - k_1 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

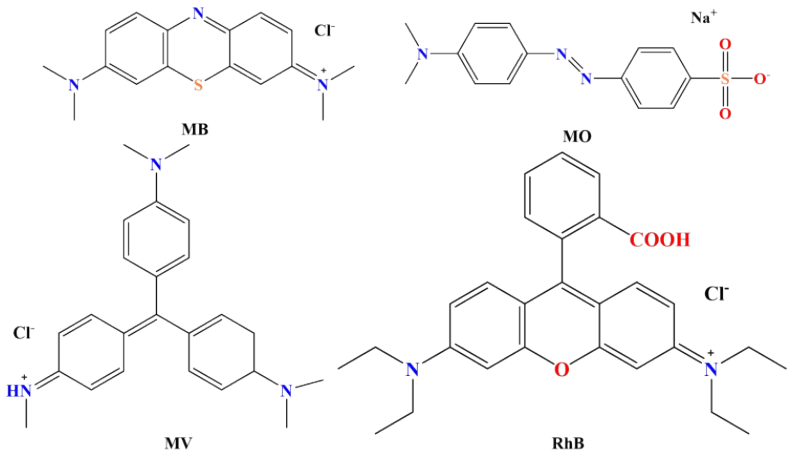
Where, q_t and q_e (mg/g) are the adsorbed amounts of dye at any time t and equilibrium, respectively; k_1 (min^{-1}) and k_2 (g/(mg·min)) are the rate constants of pseudo-first-order and pseudo-second-order.

The theoretical maximum adsorption capacity and adsorption mechanism were assessed through the Langmuir and Freundlich isotherms. Their linear forms were given below:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{K_L Q_{max}} \quad (6)$$

$$lnQ_e = lnK_F + \frac{1}{n} + lnC_e \quad (7)$$

Here, C_e represents the equilibrium concentration (mg/L) of submethyl blue after the adsorption; Q_e represents the equilibrium adsorption amount (mg/g) of the adsorbent, Q_{max} is the maximum adsorption capacity (mg/g) of the adsorbent, while K_L (L/mg) is the Langmuir constant determined by the affinity of the binding site, which defines the adsorption energy. The K_F and n_F are Freundlich constants, corresponding to the capacity and strength of adsorption, respectively. The value of 1/n determines the tendency of adsorption mechanism and the surface unevenness of adsorbent.



Scheme S2 Selected cationic dyes (MB, RhB, MV) and anionic Dyes (MO) in adsorption process.

Table S2 Different dyes relative molecular weight and molecular size.

Dye	Formula weight	Molecular dimension(Å^3)
RhB	479.02	13.43×5.35×4.93
MB	373.9	1.8×5.5×14.2
MV	408.3	4×16.32×14.15
MO	327.33	4.5×6.0×14.8

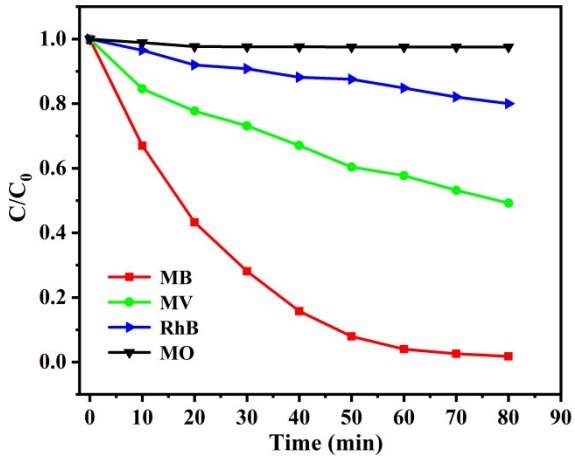


Figure S7 The absorption rate of **Zn-MOF** by different organic dyes.

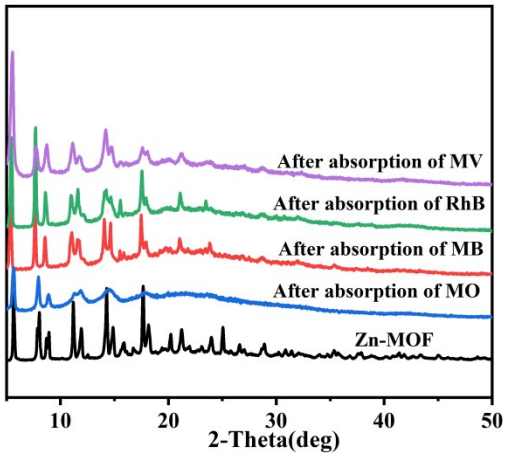


Figure S8 PXRD: Samples after dye absorption.

Table S3 Main fitting parameters of the adsorption kinetic model.

	pseudo-first-order			pseudo-second-order		
$q_{e,}$(mg/g)	k_1(min^{-1})	q_e(mg/g)	R^2	k_2(g/(mg·min))	q_e(mg/g)	R^2
30.76	0.06662	27.28	0.95411	0.00155	32.368	0.98118

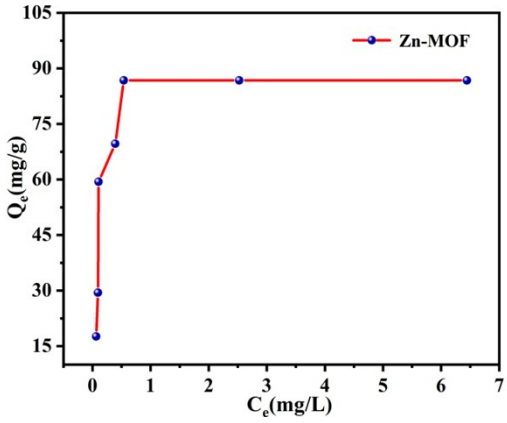


Figure S9 Adsorption isotherms of MB dye onto **Zn-MOF**.

Table S4 Isotherm constants of adsorption models for MB dye.

		Langmuir constants			Freundlich constants		
dye	absorbent	Q_{max} (mg/g)	K_L	R^2	1/n	K_F	R^2
MB	**Zn-MOF**	83.75	15.24	0.99422	0.27493	69.225	0.50461

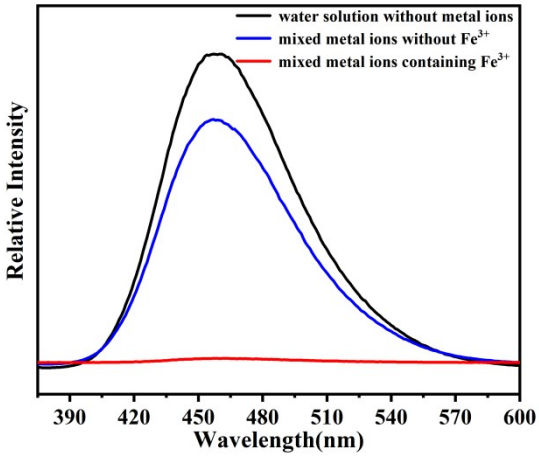


Figure S10 Fluorescence emission spectra of **Zn-MOF** in different mixed metal ion solutions.

Table S5 A comparison of various fluorescent materials used for detecting Fe^{3+}.

Fluorescent materials	Luminescent substrates	K_{sv}/M^{-1}	detection limit/M	Ref.
$\{[Cd(L)(BPDC)]\cdot 2H_2O\}_n$	Fe^{3+}	3.63×10^4	2.21×10^{-6}	22a
$[Cd_2(pbdc)(H_2O)_3]$	Fe^{3+}	1.86×10^5	-	22b
$[Zn_5(L_5)_4(trz)_2(H_2O)_2]$	Fe^{3+}	4.1×10^5	-	22c
$\{[Cd_{1.5}(DBPT)(DiPyDz)(H_2O)]\cdot 3.5H_2O\}n$	Fe^{3+}	4.78×10^5	-	22d
$[(CH_3)_2NH_2]_6[Cd_3L(H_2O)_2]\cdot 12H_2O$	Fe^{3+}	2.67×10^5	-	22e
$[Cd(bci)]\}n\cdot 2n(H_2O)$	Fe^{3+}	1.136×10^4	2.15×10^{-4}	23a
$Eu(C_{22}H_{14}O_2)_3$	Fe^{3+}	-	10^{-4}	23b
$Eu(acac)_3\subset Zn(C_{15}H_{12}NO_2)_2$	Fe^{3+}	-	5×10^{-3}	23c
Zn-MOF	Fe^{3+}	5.35×10^5	2.98×10^{-4}	This work

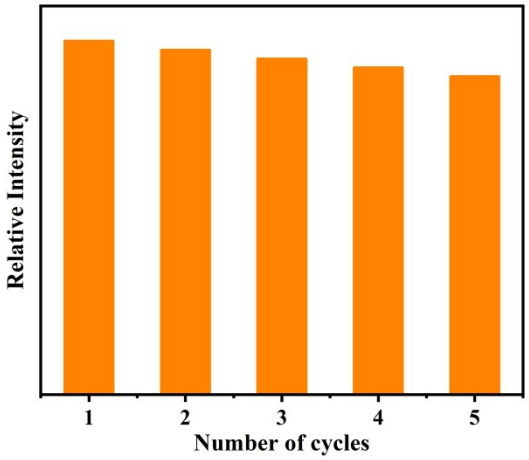


Figure S11 Multiple cycles for the fluorescence quenching of **Zn-MOF** by Fe^{3+} and recovery after washing by H_2O for several times.

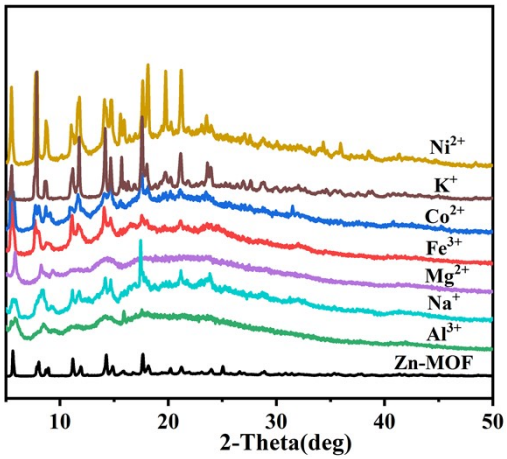


Figure S12 PXRD patterns of **Zn-MOF** immersed in different metal ion solutions.

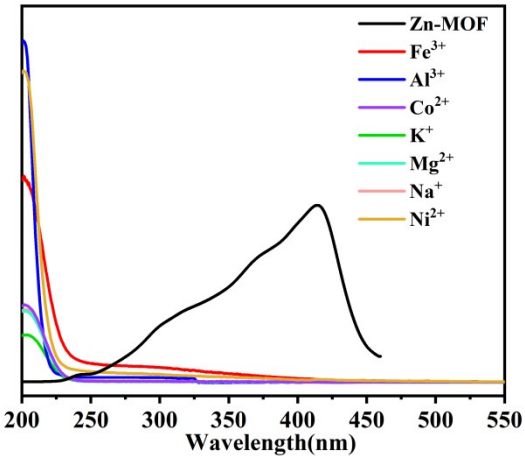


Figure S13 UV-vis adsorption spectra of $M(NO_3)_X$ aqueous and the excitation spectrum of **Zn-MOF**.

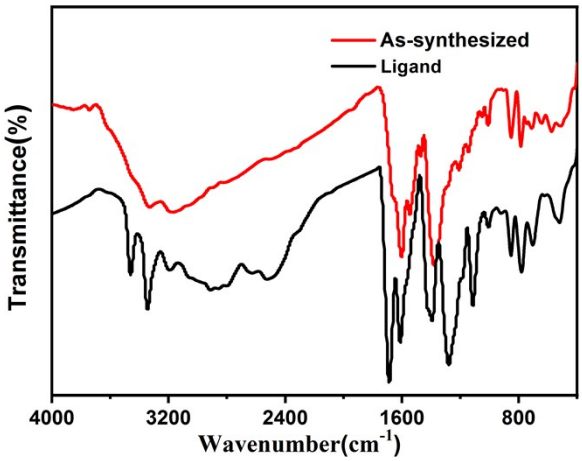


Figure S14 IR spectra of the as-synthesized **Zn-MOF** and ligand.